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Monodisperse Hollow Tricolor Pigment Particles for Electronic Paper

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Abstract A general approach has been designed to blue, green, and red pigments by metal ions doping hollow TiO_2 . The reaction involves initial formation of PS at TiO_2 core-shell nanoparticles via a mixed-solvent method, and then mixing with metal ions solution containing PEG, followed calcining in the atmosphere. The as-prepared hollow pigments exhibit uniform size, bright color, and tunable density, which are fit for electronic paper display.

Keywords E-paper · Pigment · Hollow · Bistable

Introduction

In the past few years, electronic paper (E-paper), which is a display technology based on the electrophoresis of charged particles, has recently been enthusiastically investigated with regard to not only their potential application in planar display, but also the fundamental understanding of nanoscopic phenomena [1–6]. There are many benefits over other display technologies, such as low-power consumption, good flexibility, low weight and high reflexivity and contrast [7–10].

Ever since E-paper was first prepared, the performance of electronic paper has been rapidly improved, as a result of technological development and the accumulation of fundamental knowledge. Despite tremendous advances,

one of the common challenges for all the electronic paper techniques is to achieve full-color E-paper [11]. For colorization, color filters decrease the contrast and brightness. A pixel composed of tricolor unites, in which red, blue, and green particles are suspended in a fluid medium, respectively, is a promising design. Thereby, it is necessary to prepare tricolor pigment particles. For E-paper display, the pigments should be bistable [12]. By applying the voltage, the pigments move, while stopping the voltage, it will hold still. The pigments will keep at the position until applying a voltage. In the case, the matching of the pigments with the dielectric medium is a key factor. There have been a few early attempts at achieving the objectives. It involves polymer coating on pigments or polymer-pigment hybrid [13]; however, these pigments are limited as the polymer decreases the color gamut. In this article, a solution for the problem will be given while we prepare hollow pigments.

Here, a facile general method, which is based on the tuning of the bandgap of semiconductor by metal ions doping is developed to prepare monodisperse hollow tricolor pigment particles. Titania and Cr^{2+} metal ions are selected as host materials and dopants, respectively. The obtained green hollow pigment samples (Cr^{3+} doped TiO_2), are well characterized by using X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), and UV-vis diffuse reflection. They show brilliant colors in visible region. And the density of hollow pigment particles is about 1.32 g/cm^3 , which is very low and can match well with most of dispersants. By the method, we can also prepare other metal ions doped TiO_2 hollow nanocomposites, such as Co/Al doped TiO_2 hollow particles (blue), Fe doped TiO_2 hollow particles (red). The monodisperse hollow tricolor pigment particles are potential building blocks to fabricate full-color electrophoretic display.

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Fig. 1 The TEM and SEM images pure PS particles (a), the PS/TiO₂ hybrid particles (b) and the TEM and SEM the Cr³⁺-doped TiO₂ hollow particles (c and d)

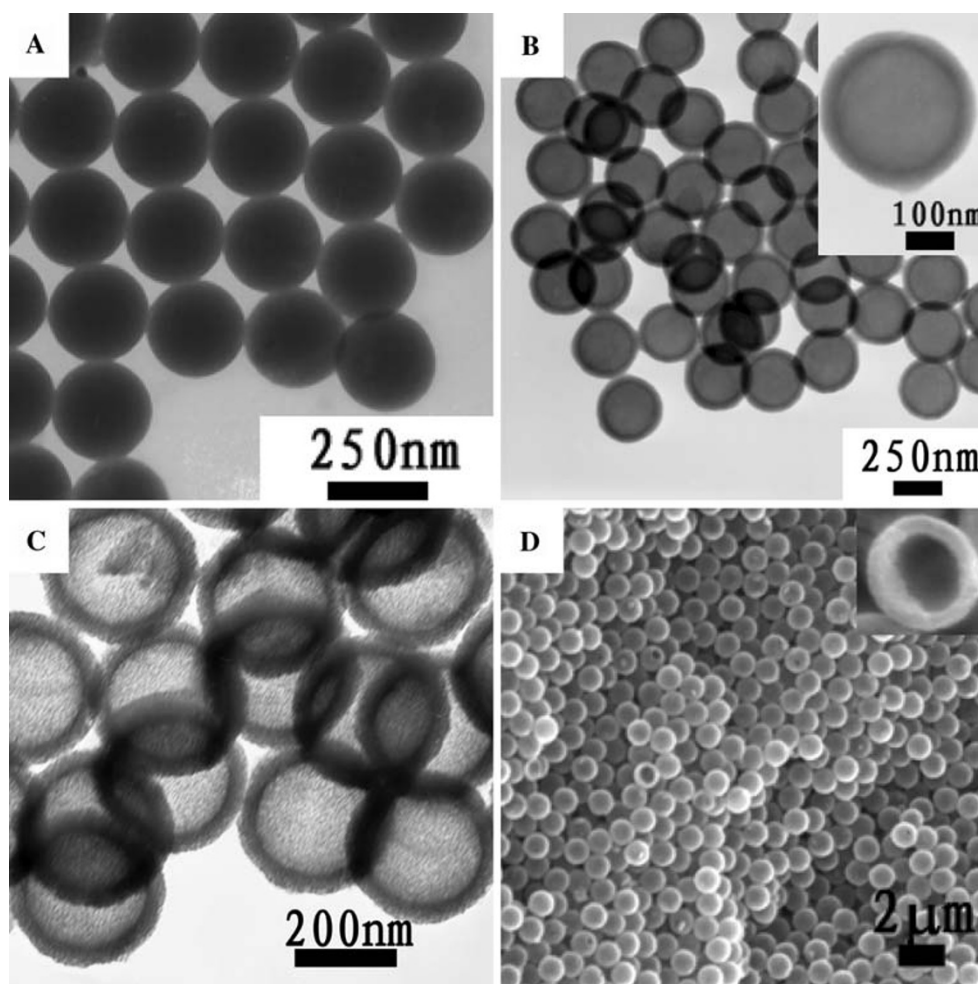
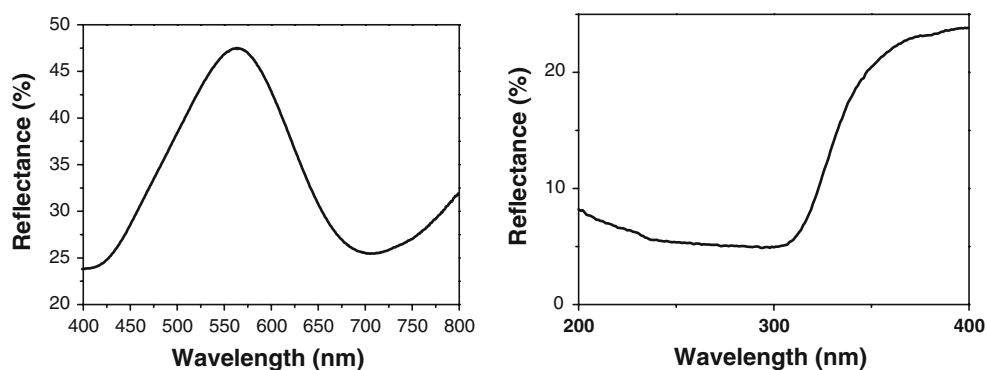


Fig. 2 The reflection spectrum of monodisperse hollow Cr³⁺-doped TiO₂ particles



Experimental

Tetra-*n*-butyl titanate (TBT) and acetonitrile were purchased from Sigma and used without further purification. Potassium persulfate (KPS), FeCl₃·6H₂O, CrCl₃·6H₂O, Al (NO₃)₃·9H₂O, Polyethylene glycol (PEG 10000), styrene, ethanol, and ammonia were all supplied by the

Beijing Chemical Reagent Company. Styrene was purified by distillation under reduced pressure. Ethanol was dehydrated by molecule sieves.

The monodisperse metal ions doped TiO₂ hollow particles were prepared by using the Pechini sol-gel process. Anionic polystyrene (PS) spheres used as core materials were prepared by emulsifier-free, emulsion polymerization

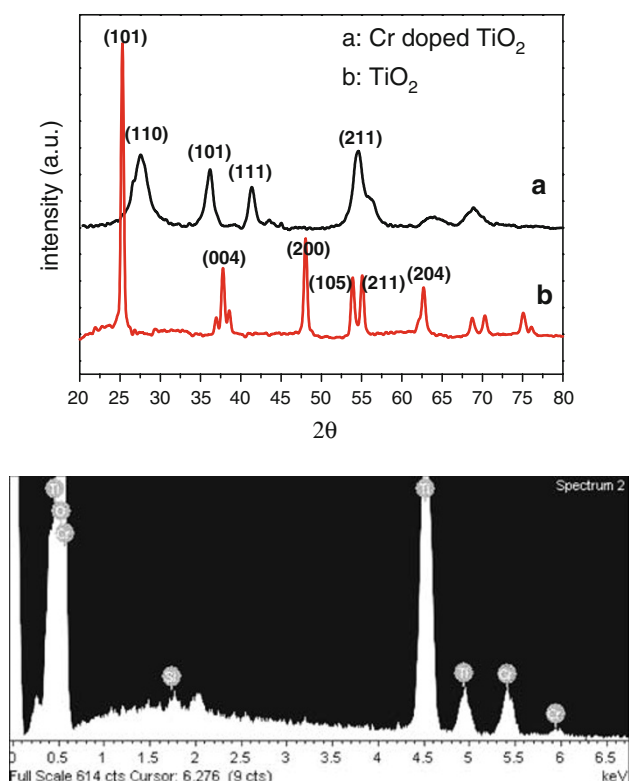


Fig. 3 XRD profile of Cr^{3+} doped (a) and TiO_2 hollow particles (b). And the EDX spectra of the Cr^{3+} -doped TiO_2 hollow particles

using KPS as the anionic initiator. TiO_2 coating on the as-prepared PS core was processed in the mixed solvent of ethanol and acetonitrile by hydrolyzing TBT in the presence of ammonia, as described in our previous report [14]. 1.2 mmol $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was first dissolved in a water–ethanol (1/7 v/v) solution containing citric acid which was two times as much as the metal ions in amount of substance. And then a certain amount of the PEG (10000) was added. The solution was stirred for 2 h and then the above PS/ TiO_2 hybrid spheres (0.04 g) were added. After stirring for another 4 h, the particles were separated by centrifugation. The samples were dried at 60 °C for 2 h and then annealed at 500 °C for 4 h with a heating rate of 5 °C/min. Finally the preheated samples were annealed at 600 °C for 2 h with a heating rate of 2 °C/min.

TEM (JEOL-200CX) and SEM (Hitachi 4300) were used to observe the morphology of the particles. XRD measurement was employed a Japan Regaku D/max γA X-ray diffractometer equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) irradiated with a scanning rate of 0.02 deg/s. Ultraviolet and visible absorption (UV–vis) and diffuse reflectance spectra were recorded at room temperature with the JASCO 570 spectrophotometer equipped with an integrated sphere.

Results and Discussion

E-paper is a straightforward fusion of chemistry, physics, and electronics. The pigments are very important to the E-paper properties [15–17]. In the interest of a full-color electronic paper, the tricolor particles are required. For green hollow nanospheres, PS at TiO_2 core–shell nanoparticles are synthesized by a mixed-solvent method, and then mixed with Cr^{3+} ions in the solution containing PEG, followed calcined in the atmosphere. The monodisperse Cr^{3+} -doped TiO_2 hollow particles are prepared by using the Pechini sol–gel process by varying the condition, such as ratio of Cr^{3+} ions to PS at TiO_2 and the concentration of PEG. During the reaction, the chelate complexes of metal ions react with PEG to form polyesters with suitable viscosity, which coat on the surfaces of the PS/ TiO_2 particles.

Figure 1 shows the TEM and SEM images of the Cr^{3+} -doped TiO_2 hollow particles. The morphology of the pure PS particles (about 250 nm) (Fig. 1a) and the PS/ TiO_2 hybrid particles (about 320 nm) (Fig. 1b) is presented. It can be seen that a well-defined core–shell structure with PS particle as core and TiO_2 as shell has been formed. The inset in Fig. 1b shows the detailed structure. Typically, Fig. 1c and d shows the TEM and SEM images of Cr^{3+} -doped TiO_2 hollow particles with uniform size and shape. The size of all the hollow particles is about 300 nm and shells are compact and the shells are uniform, intact, and about 35 nm thick. From the inset in Fig. 1d, we can find the hollow hemisphere is vivid.

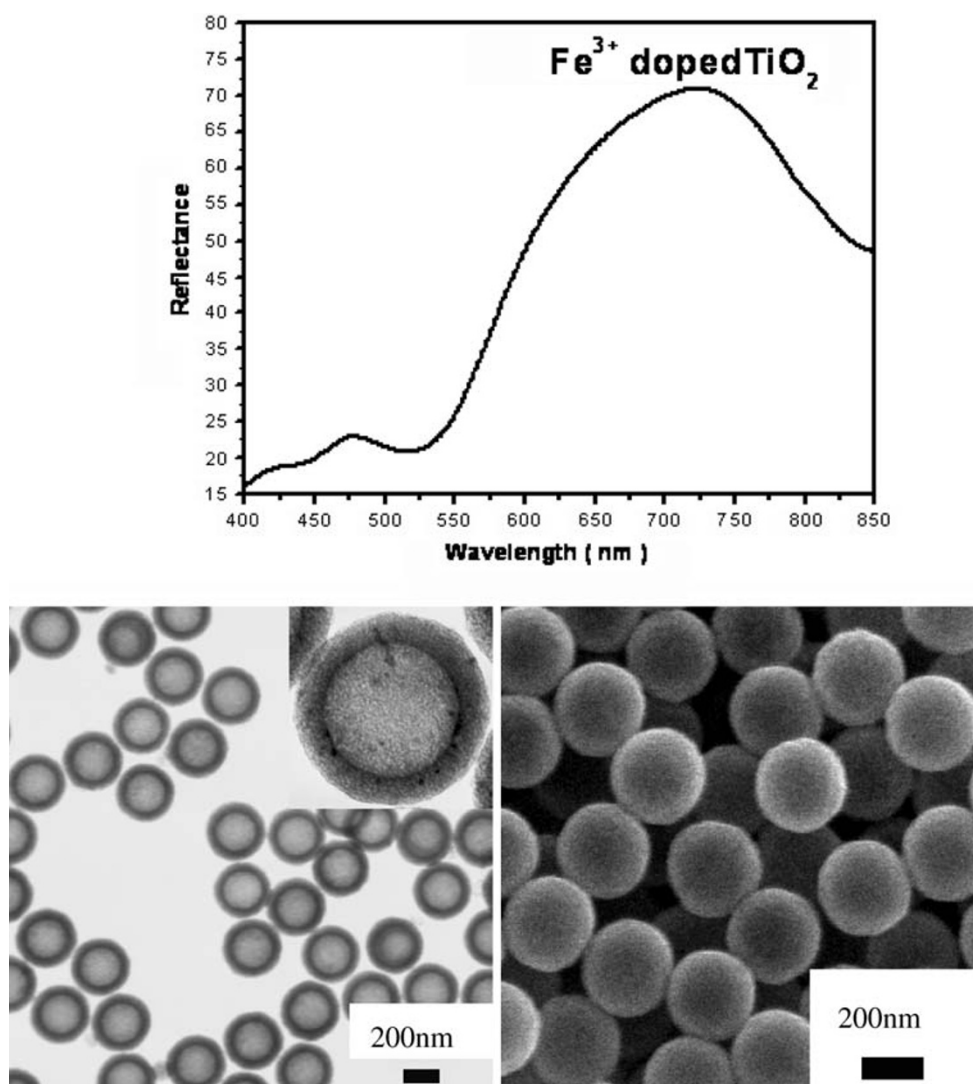
The uniform hollow particle is an ideal candidate for E-paper pigments. During the moving of pigment, the electrophoretic velocity (v) is governed by the following equation [18]:

$$v = QE/4\pi r\eta$$

where Q , r , η , and E represent the charge, particle radius, viscosity of the suspension, and the potential difference applied to the suspension, respectively. The suspension viscosity can be considered constant in suspension. Under this condition, the electrophoretic velocity is mainly a function of the electric field and the particle size. As the particles in the suspension used for E-paper usually have a distribution of particle sizes, particles with different r value have different electrophoretic mobility, thereby resulting in the segregation effects observed during the display process. From the equation, we know that the particles with the same size shuttle between the up and down side of a pixel simultaneously. Thus, the uniform Cr^{3+} -doped TiO_2 hollow particles will improve display properties.

As shown in Fig. 2, the reflection spectra of the hollow particles are measured. It can be seen that the peak for Cr^{3+} -doped TiO_2 hollow particles in the visible region

Fig. 4 The TEM and SEM images, and the reflection spectrum of Fe^{3+} -doped red hollow particles



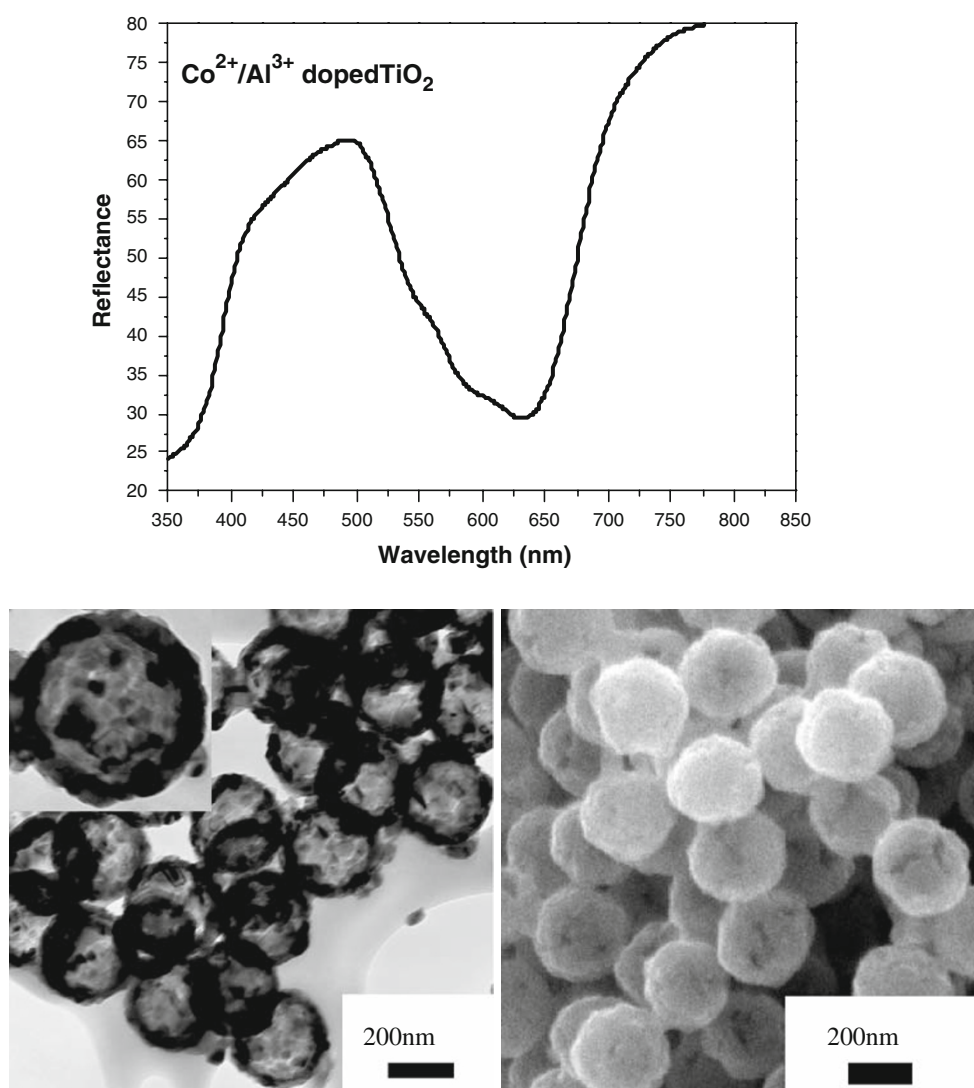
are 570 nm. And the reflection edges of most samples are somewhat steep, indicating brilliant colors of the hollow particles. The suspension of the hollow particles in ethylene glycol shows yellow green, shown in the inset in Fig. 2b, which implies that Cr^{3+} -doped TiO_2 hollow particles could be used as excellent pigments. And the reflectance in ultraviolet B range is very low, between 4.9 and 8.7% (Fig. 2b).

To verify the compositions of the obtained multifunctional hollow nanocomposites, the energy-dispersive X-ray (EDX) spectrums of Cr^{3+} -doped TiO_2 hollow particles is recorded (Fig. 3). And O, Ti, Cr, and Si peaks for doped TiO_2 are observed (silicon signal from the silicon substrate). These results indicate that the hollow Cr^{3+} -doped TiO_2 nanocomposites are synthesized successfully. Figure 3b shows the typical XRD patterns of Cr^{3+} -doped TiO_2 hollow particles and TiO_2 hollow particles. All of the

detectable peaks of Cr^{3+} -doped TiO_2 can be indexed as the TiO_2 with rutile structure (Fig. 3a). And the peaks corresponding to 27.3° , 35.9° , 41.1° , and 54.1° are in good agreement with (110), (101), (111), and (211) planes of the rutile (rutile phases JCPDS 77-0443). But the XRD patterns of TiO_2 hollow particles without any dopants obtained under the same conditions consist of anatase (Fig. 3b). And the peaks corresponding to 25.3° , 37.8° , 48° , 53.9° , 55° , and 62.7° can be assigned to (101), (004), (200), (105), (211), and (204) planes of the rutile (rutile phases JCPDS 77-0443). This indicates that the substitution metal ions for Ti have promoted the A-R phase transition. Thereby, the hollow particles do not only show brilliant colors, but also high stability in ultraviolet and visible region.

When Fe^{3+} , Co^{2+} , and Al^{3+} ions are used as the starting materials, red (Fig. 4) and blue (Fig. 5) metal-doped

Fig. 5 The TEM and SEM images, and the reflection spectrum of $\text{Co}^{2+}/\text{Al}^{3+}$ -doped blue hollow particles



hollow particles are synthesized. The inorganic pigments can be used as full-color E-paper display.

Conclusions

The monodisperse Cr^{3+} -doped TiO_2 hollow particles are prepared by using the Pechini sol–gel process, in which PS at TiO_2 core–shell nanoparticles are synthesized by a mixed-solvent method, and then mixed with Cr^{3+} in the solution containing PEG, followed calcined in the atmosphere. Fe^{3+} -doped TiO_2 (red) and $\text{Co}^{2+}/\text{Al}^{3+}$ -doped TiO_2 (blue) hollow nanocomposites are also prepared by this method. The hollow pigments are good candidates for full-color E-paper display.

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